Substance name: 4,4'-Diaminodiphenylmethane (MDA)
EC number: 202-974-4
CAS number: 101-77-9

PRIORITISATION AND ANNEX XIV BACKGROUND INFORMATION

14 January 2009

Disclaimer:

The present document has been developed by ECHA mainly based on the technical report "Data on Manufacture, Import, Export, Uses and Releases of 4,4' diaminodiphenylmethane as well as Information on Potential Alternatives to its Use"; prepared by Entec under framework contract ECHA/2008/2 (specific contract ECHA/2008/02/SR5/ECA.227). Secondary source has been the European Union Risk Assessment report (RAR 2008).

Note that the information on alternatives is not intended to be an exhaustive analysis, but is only included in order to support the transitional arrangements and in particular the proposed application dates for substances proposed to be included in Annex XIV.

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PRIORITISATION AND ANNEX XIV BACKGROUND INFORMATION

1 Prioritisation

Given the relatively high volume of MDA supplied to uses and applications that must be considered as wide dispersive, **it is proposed to prioritise 4,4'-Diamino diphenyl methane for inclusion in Annex XIV**.

2 Identity of the substance

Chemical name: 4,4'-Diaminodiphenylmethane (MDA)
EC Number: 202-974-4
CAS Number: 101-77-9
IUPAC Name: Bis (4-aminophenyl)methane

3 Intrinsic properties

The substance has been identified as a Substance of Very High Concern according to article 57(a) as it is classified as Carcinogenic, Category 2 as reported in the support document on 4,4'-Diaminodiphenylmethane (MDA) and the agreement of the MSC adopted on the 1st of October 2008.

4 Volume(s)

According to the EU Risk Assessment Report (EC, 2001), in 1993, the production capacity of 4,4'-methylene diphenyl diisocyanate (MDI), the subsequent product of MDA was estimated to be 540,000t in Western Europe. For this, about 432,000 t of MDA were needed. Since then, there has been a significant increase in volumes of MDI (and hence MDA) manufactured in the EU. Anecdotal information from industry suggests that the current production of MDA is around 3-4 times higher than in 1993 (corresponding to an approximately 8% annual compound growth) and is therefore estimated to amount to 1,400,000 t/y (ENTEC, 2008).
The use of MDA as intermediate in the synthesis of MDI represents more than 98% of the total production volume. Apart from this use the EU RAR (EC, 2001) also identifies non-MDI uses for which the annual tonnage is estimated to be more than 4000 t/y. This tonnage includes other intermediate uses than the synthesis of MDI, such as intermediate in the manufacture of high performance polymers and processing to 4-4' methylenebis(cyclohexaneamine). New information on the non-MDI intermediate use in the manufacture of high performance polymers and processing to 4-4'methylenebis(cyclohexaneamine) indicates that less than 5000 t/y of MDA is used. Regarding the non intermediate uses no information on the quantities of MDA used as hardener in adhesives is available. It is estimated by one company that the overall EU consumption of MDA as hardener in epoxy resins is around 200 t/y, however this figure should be regarded as a minimum. Furthermore, at least 150t/y of MDA is used exclusively for another application of hardener in epoxy resins.

In conclusion, the production of MDA for non intermediate uses is estimated to be around 350 t/y but this volume should be regarded as a minimum as it does not include the amount of MDA used as hardener in adhesives and the figure for the use of MDA as hardener in epoxy resins might be underestimated.

5 Characterisation of uses and releases

5.1 Manufacture and uses

As stated above the EU RAR (EC, 2001) indicated that more than 98% of the total production of MDA was used on-site as an intermediate for the production of 4,4´-methylene diphenyl diisocyanate (MDI). MDI is further used for polyurethane production. Given the significant increase in MDA/MDI production, it is considered likely that the percentage used in MDA production is at least 98% and may well be greater (ENTEC, 2008).

Apart from its use in the synthesis of MDI, the RAR (EC, 2001) identifies the following uses for MDA:

- Intermediate in the manufacture of high performance polymers
- Processing to 4-4'methylenebis(cyclohexaneamine) used as a hardener in epoxy resins.
- Hardener in epoxy resins
- Hardener in adhesives

Based on the information from the Nordic product registers it is assumed that for the period between 2000 and 2006 the overall European consumption of MDA in non-MDI uses remained fairly constant (at least within an order of magnitude). Therefore it is assumed that the figure of 4000 t/y used in the EU RAR (EC, 2001) is still valid or is at least within an order of magnitude.

The first two uses (intermediate in the manufacture of high performance polymers and processing to 4-4'methylenebis(cyclohexaneamine) used as a hardener in epoxy resins) are intermediate uses. There is no information available on the quantities of MDA used in the processing to 4-4' methylenebis(cyclohexaneamine), however some data from one producer indicates that for the use as intermediate in the manufacture of high performance polymers less than 5000 t/y of MDA is used.

Regarding the use of MDA as hardener in epoxy resins, the available information indicates that MDA is used as a hardener in epoxy resins curing agents for coatings as well as a hardener for the manufacture of pipes using filament winding process. The tonnage values available indicate that at least 200 t/y of MDA are used as a hardener in epoxy resins curing agent and at least 150t/y of MDA is used exclusively in the filament wound pipe application.

The information available on the use of MDA as hardener in adhesives indicates that MDA is not likely to be used in adhesives or is being phased out from that use. MDA-containing hardener is still used in the automotive industry in binders for 'sand forms'

to cast engine parts. No information on the quantities of MDA used as hardener in adhesives is available.

No amount is available on EU import and export volumes of MDA. MDA is imported by some manufacturers as finished curing systems containing MDA. In addition, it seems that at least one company acts as a distributor and imports and exports MDA from/to the EU.

5.2 Releases

Releases of MDA into the environment from non-intermediate uses (hardener in epoxy resins and adhesives) are considered not to be significant (EC, 2001).
However releases are expected from these uses resulting in exposure of the workers in the skilled trade area (small and medium-sized companies). It seems that some companies do not sell epoxy resins curing agents containing MDA to the skilled trade area and that these products are intended to be applied in an industrial environment. However it is unclear if this is the case for all the companies dealing with curing agents containing MDA.
Regarding the hardener in adhesives containing MDA no information is available.

As a consequence it can not be excluded that there might be exposure of workers in the skilled trade area due to the use of hardener in epoxy resins and adhesives containing MDA.

5.3 Geographical distribution

ISOPA (the European trade association for producers of diisocyanates and polyols) has indicated that there are currently 5 or 6 companies producing MDA and MDI in the EU but the number and location of the sites is unknown. In the EU RAR (EC, 2001) 10 producing sites were reported for 1989.
It is expected however, that there are manufacturing facilities in several Member States and therefore releases from manufacture are considered to be geographically widespread across a number of point sources in the EU.

The non-intermediate use of MDA as hardener in epoxy resins and hardener in adhesives is expected to occur potentially across the entire EU and might result in exposure of the workers in the skilled trade area (small and medium sized companies).

5.4 Conclusions on wide dispersiveness of uses

The uses as hardener in epoxy resins and adhesives are expected to potentially occur across the entire EU and are therefore considered to be widespread. Furthermore releases to the working environment and as a consequence exposure of workers in the skilled trade area cannot be excluded. The uses of MDA as hardener in epoxy resins and adhesives in the skilled trade area are therefore considered to be wide dispersive.

6 Complexity of the supply chain

MDA is mainly used as an on-site intermediate, in a rather limited number of sites throughout the EU.

According to the available information, the only non-intermediate uses of MDA are as hardener in epoxy resins and adhesives. According to available information the involved supply-chains appear to be rather short. The use of MDA as a hardener in epoxy resins and adhesives may potentially involve a high number of professional and industrial actors, however, within a limited number of relatively similar industrial sectors and professional user groups.

7 Alternatives

The use of MDA in adhesives has been phased out some time ago (8-15 years) by a number of companies, therefore it is thought that alternatives have been developed. No information on the alternatives used was disclosed. However it was indicated that each alternative was product or application – specific.

Regarding the availability of alternatives for the use of MDA as hardener in epoxy resins, it seems that the difficulty in finding alternatives to MDA is in the need to reduce the hazardous potential of those alternatives which are often aromatic amines and potential carcinogen. Consequently, some suitable alternatives are available but their application to some uses might be limited.

8 Existing Community legislation relevant for possible exemptions

MDA is restricted in accordance with Directive 76/769/EEC as follows:

Entry 30: Substances which appear in Annex I to Directive 67/548/EEC classified as toxic to reproduction category 1 or 2, shall not be placed on the market for supply to the general public as a substance on its own or in preparations when the individual concentration is equal to or greater than 0.5%. This does not apply to medicinal or veterinary products, cosmetic products, motor fuels, mineral oil products intended for use as fuel, fuels sold in closed systems, and artists' paints.

However, it should be noted that there is no available information indicating that MDA would currently (or could technically) be used in artists' paints.

9 Other information

Not available.

10 References

EC, 2001. Risk-Assessment Report Vol.09, November 2000 on 4,4'-methylenedianiline, CAS#: 101-77-9, EINECS#: 231-634-8. Publication: EUR 19727 EN

ENTEC, 2008. Data on manufacture, import, export, uses and releases of 4,4' diaminodiphenylmethane as well as information on potential alternatives to its use. (ECHA/2008/02SR5/ECA.227)